Available online at www.sciencedirect.com

SciVerse ScienceDirect

Procedia Engineering 44 (2012) 948 – 949

Procedia Engineering

www.elsevier.com/locate/procedia

Euromembrane Conference 2012

[P1.111]

Transport properties and submolecular organization in high permeable 1,2-disubstituted polyacetylenes

S.M. Matson*[1], E.G. Litvinova[1], E.Y. Sultanov[1], A.A. Ezhov[2], V.S. Khotimskiy[1]

[1]RAS, Russia, [2]Moscow State University, Russia

Amorphous glassy 1,2-disubstituted polyacetylenes show unique transport properties, namely exceptionally high permeability and a high organic vapor/permanent gas selectivity. Silicon-containing disubstituted polyacetylene poly(1-trimethylsilyl-1-propyne) (PTMSP) exhibits the highest gas and organic vapor permeability and selectivity during recovery of C_{3+} from permanent gas.

Unique properties of disubstituted polyacetylenes are provided by a specific organization of nanospace in these polymers, namely, extremely high fractional free volume and interconnected free volume elements. The specific structure is formed by rigid backbone containing C=C bonds and bulky substituents.

The main chain of 1,2-disubstituted polyacetylenes contains alternating double bonds and therefore may have various geometric structures, i.e. units in *cis*- and *trans*-configuration. Detailed investigation of synthesis of poly(1-trimethylsilyl-1-propyne) (PTMSP) and its Ge-containing analogue poly(1-trimethylgermyl-1-propyne) (PTMGP) in the presence of catalytic systems based on Nb and Ta pentachlorides has shown that by varying synthesis conditions, e.g. cocatalyst, solvent polarity and temperature of polymerization process one can regulate the geometric structure of macrochains, i.e. the ratio of *cis*- and *trans*-units, that determines submolecular organization of the polymer. It was shown that functional properties of disubstituted polyacetylenes such as transport characteristics, as well as stability towards organic solvents are controlled by the geometric structure. Subtle variation in packing of polymer chains with different microstructure can alter the polymer submolecular organization and thus influencing free volume structure. Therefore, the investigation of the free volume structure is very important for understanding the relation between polymer structure and its properties.

In this study the correlation between polymer microstructure, submolecular structure and transport parameters for high permeable disubstituted polyacetylenes are discussed. Disubstituted polyacetylenes PTMSP, PTMGP and poly(4-methyl-2-pentyne) (PMP) with different specific geometric structure (calculated from the ^{13}C NMR spectra) were synthesized by methods of regulated stereospecific polymerization with the use of catalytic systems based on Nb and Ta pentachlorides.

Gas transport properties of synthesized polymers were tested using individual gases (O_2, N_2, methane and *n*-butane) as well as a mixtures of *n*-butane/methane (content of *n*-butane 1.6 and 4.5 mol.%). Pure gas as well as mixed gas permeability and *n*-butane/methane selectivity significantly differ for polymers with various geometric structure. Polymers with *trans*-enriched microstructure show significantly higher permeability and *n*-butane/methane selectivity.

Differences of gas transport parameters for investigated polymers with different geometric structure indicate on dissimilarity in packing of macromolecules containing different *cis-/trans*-units ratios. The surface topography of polymer films, studied by AFM, consists of clusters with different lateral size. The correlation was observed between increasing the size of cluster and enhancement of permeability as well as a mixed *n*-butane/methane selectivity. Earlier in our investigations was shown that high-free-volume disubstituted polyacetylenes have a two-phase structure characterized by the presence of regions with an enhanced level of ordering dispersed in amorphous polymer matrix. The different submolecular structure in polymers may be associated with both different lengths of continuous sequences of units of the

doi:10.1016/j.proeng.2012.08.631

same geometry and different thermodynamic flexibilities of macromolecules, that both determine the size of clusters. The size of clusters influence on polymer packing density which governs gas transport through polymer matrix.

Differences in submolecular structure of polymers with different geometric structure was confirmed by low-temperature nitrogen adsorption BET measurements. According to N2 BET measurements the sorption capacity as well as the surface area of polymers with higher permeability and mixed *n*-butane/methane selectivity is greater than for polymers with lower permeability.

PALS investigation of polymers that have the same chemical structure but different *cis-/trans-* composition revealed differences in total amount and structure of free volume. It was observed that polymers with bigger total free volume demonstrate higher *n*-butane permeability as well as *n*-butane/methane mixed-gas selectivity. That correlation can be rationalized from the view point that higher free volume facilitates better sorption of more condensable *n*-butane in free volume elements leading to blocking of methane permeation according to the selective surface sorption mechanism.

The authors gratefully acknowledge S.Shishatskiy and K.Buhr (Institute of Polymer Research, Helmholtz-Zentrum Geestacht) for assistance in gas permeations measurements. The work was financially supported by Russian Foundation for Basic Research (project 11-03-00343).

Keywords: 1,2-disubstituted polyacetylenes, microstructure, structure-property relations, transport properties